

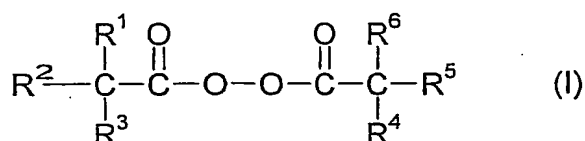
Claims

1. Polymerization process for preparing a (co)polymer wherein one or more organic peroxides selected from the group consisting of diacyl peroxides, peroxyesters, peroxydicarbonates, and mixtures thereof are used in conjunction with an effective amount of one or more organic peroxide stabilizing additives (controlling agents) selected from the group consisting of organic hydroperoxides, ethylenically unsaturated organic compounds that preferably cannot homopolymerize, compounds with labile carbon-hydrogen bonds, oximes, and mixtures thereof, with the proviso that the solubility of the peroxydicarbonate(s) in water at 0°C is at least 5 ppm, preferably the solubility of all organic peroxides in water at 0°C is at least 5 ppm, and wherein the process is a conventional aqueous dispersion polymerization process or an aqueous dispersion polymerization process wherein at least part of the one or more organic peroxides used as initiator is dosed to the reaction mixture at the polymerization temperature.
2. A polymerization process according to claim 1 wherein the one or more organic peroxides are selected from the group of diacyl peroxides, peroxyesters, and mixtures thereof
3. A polymerization process according to claim 2 wherein the one or more organic peroxides have a solubility in water at 0°C of at least 5 ppm
4. A polymerization process according to any one of claims 1 to 3 wherein the one or more organic peroxides are selected from the group consisting of organic peroxides having a half-life of at least 0.0001 hour and at most 1.0 hour at the polymerization temperature and mixtures thereof

5. A process according to any one of claims 1-4 wherein the organic peroxide used as initiator is dosed continuously and/or intermittently to the reaction mixture.
- 5 6. A process according to any one of claims 1-5 wherein the controlling agent is an organic hydroperoxide or an ethylenically unsaturated organic compound that preferably cannot homopolymerize.
- 10 7. A process according to any one of claims 1-6 wherein the controlling agent is an organic hydroperoxide or a mixture of organic hydroperoxides, said organic hydroperoxide having the general formula ROOH , wherein R represents an organic group, more particularly R represents a branched or non-branched, substituted or unsubstituted alkyl group, alkenyl group, alkynyl group or cycloalkyl group, preferably wherein the organic
- 15 hydroperoxide is a tertiary hydroperoxide selected from the group of tert-butyl hydroperoxide, tert-amyl hydroperoxide, 1,1,3,3-tetramethylbutyl hydroperoxide, 2-hydroperoxy-2-methyl pentane, 2-hydroperoxy-2-methyl-3-butene, 2-hydroperoxy-2,4,4-trimethyl pentane, 2,5-dihydroperoxy-2,5-dimethyl hexane, 2,5-dihydroperoxy-2,5-dimethyl-3-hexyn, 2,6-dihydro-
- 20 peroxy-4-hydroxy-2,6-dimethyl heptane, 2-hydroperoxy-4-hydroxy-2-methyl butane, 2-hydroperoxy-4-hydroxy-2-methyl pentane, 2-hydroperoxy-4-hydroxy-2-methyl heptane, 3-ethyl-3-hydroperoxy-5-hydroxy hexane, cumyl hydroperoxide (2-phenyl-2-hydroperoxy propane), m- and p-isopropylcumyl hydroperoxide, m- and p-(tert-butylperoxy isopropyl)cumyl hydroperoxide, 1-
- 25 hydroperoxy-1-methyl cyclohexane, 1-hydroperoxy-5-hydroxy-1,3,3-trimethyl cyclohexane, p-menthane hydroperoxide, and pinane hydroperoxide, the organic hydroperoxide most preferably being selected from tert-butyl hydroperoxide, tert-amyl hydroperoxide, and 1,1,3,3-tetramethylbutyl hydroperoxide.

8. A process according to any one of claims 1-7 wherein the diacyl peroxides, peroxyesters, and/or peroxydicarbonates are selected from the group consisting of:

- diacyl peroxides of formula (I)



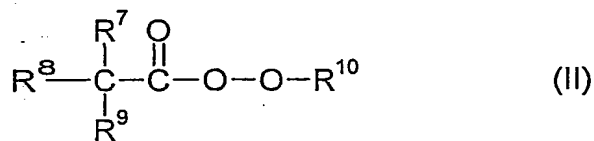
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wherein R¹-R⁶ are independently selected from the group consisting of hydrogen, halogens, alkoxy groups, and saturated or unsaturated, linear or branched, substituted or unsubstituted alkyl, alkaryl, and aralkyl moieties, and wherein two of R¹-R³ of R¹C(R²)R³ and/or two of R⁴-R⁶ of R⁴C(R⁵)R⁶ can be linked to form a cyclic structure which can be saturated or unsaturated and optionally may be substituted with one or more independently chosen groups R²⁸, which R²⁸ is selected from the group consisting of hydrogen, halogens, alkoxy groups, and saturated or unsaturated, linear or branched, substituted or unsubstituted alkyl, alkaryl, and aralkyl moieties, with the proviso that at most one of R¹C(R²)R³ and R⁴C(R⁵)R⁶ is CH₃,

- peroxyesters of formula (II)

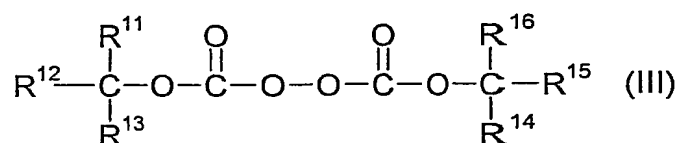


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wherein R⁷-R⁹ are independently selected from the group consisting of hydrogen, halogens, alkoxy groups, and saturated or unsaturated, linear or branched, substituted or unsubstituted alkyl, alkaryl, and aralkyl moieties, with the proviso that R⁷C(R⁸)R⁹ is not CH₃, wherein two of R⁷-R⁹ can be linked to form a cyclic structure which can be saturated or unsaturated and optionally may be substituted with one or more

- independently chosen groups R^{29} , which R^{29} is selected from the group consisting of hydrogen, halogens, alkoxy groups, and saturated or unsaturated, linear or branched, substituted or unsubstituted alkyl, alkaryl, and aralkyl moieties, and wherein R^{10} is selected from the group consisting of saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl, alkaryl, and aralkyl moieties, and
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- peroxydicarbonates of formula (III)



- wherein R^{11} - R^{16} are independently selected from the group consisting of hydrogen, halogens, and saturated or unsaturated alkyl moieties wherein the number of carbon atoms is at most 4, and wherein two of R^{11} - R^{13} of $R^{11}C(R^{12})R^{13}$ and/or two of R^{14} - R^{16} can be linked to form a cyclic structure which can be saturated or unsaturated and optionally may be substituted with one or more independently chosen groups R^{30} , which
- 10
- R^{30} is selected from the group consisting of hydrogen, halogens, alkoxy groups, and saturated or unsaturated, linear or branched, substituted or unsubstituted alkyl, alkaryl, and aralkyl moieties.
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9. A process according to any one of claims 1-8 wherein the organic peroxide
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- is diisobutyl peroxide and the controlling agent is tert-butyl hydroperoxide.
10. A process according to any one of claims 1-9 wherein the controlling agent is dosed to the polymerization process in the form of a composition further comprising one or more organic peroxides selected from the group consisting of diacyl peroxides, peroxyesters, peroxydicarbonates, and
- 25
- mixtures thereof.

11. A process according to any one of claims 4-10 wherein the organic peroxide has a half-life of at most 0.8 hours at the polymerization temperature, more preferably of at most 0.5 hours, and most preferably of at most 0.3 hours.

5 12. (Co)polymer obtainable by the process of any one of preceding claims 1-11.

13. Formulation suitable for use in an aqueous dispersion polymerization process of any one of preceding claims 8-11, said formulation comprising one or more organic peroxides selected from the group consisting of diacyl peroxides of formula I and an effective amount of dibutyl maleate as
10 controlling agent.

14. Formulation suitable for use in an aqueous dispersion polymerization process of any one of preceding claims 8-11, said formulation comprising
15 one or more organic peroxides selected from the group of diacyl peroxides of formula I as described above, peroxyesters of formula II as described above, and mixtures thereof, and an effective amount of an organic hydroperoxide as controlling agent, provided that it does not relate to a formulation comprising a peroxide of the formula $R-O-C(O)-O-O-C(O)-O-R'$ wherein R and R' are independently selected from branched or non-
20 branched, substituted or unsubstituted, alkyl, alkenyl or cycloalkyl C_1-C_{20} hydrocarbon moieties and a phlegmatizing agent according to the formula $R''HC=CHR'''$, wherein R'' and R''' are independently selected from hydrogen and the group consisting of linear or branched, substituted or unsubstituted,
25 saturated or unsaturated C_1-C_{12} alkane moieties and R'' and R''' may be connected to form a cyclic structure.